# ADVANCED BINDERS FOR SOLID PROPELLANTS - A REVIEW

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The earliest known use of solid propellants dates from reports of Chinese military rockets in the 13th Century. From that period up until relatively recent times the composition of solid propellants remained essentially constant, that is, a mixture of loose powder containing sulfur, nitrate salts and carbon (charcoal). A composition of this type could never be developed for a major role in propulsion because by its very nature it could not give reliable ballistic properties nor could it be used in large diameter (high thrust) motors. With the advent of World War II, smokeless powder or double base gunpowder was adapted to propelling rockets. Here again loose powder mixtures were first used with many of the previously mentioned limitations. Consolidation of the loose powders into homogeneous forms or grains was a major development in double base technology. The colloidal solution of the polymer, nitrocellulose, in the plasticizer, nitroglycerin, gave a solid mass or grain which could be molded to conform to a wide range of motor geometries and be used to deliver long duration thrust in a programmed manner. Early efforts at the development of castable composite systems were pioneered by the Jet Propulsion Laboratories and further developed by the Aerojet, Thiokol and Atlantic Research Companies. The earliest of the composites were asphalt-perchlorate, followed by polystyrene-perchlorate, then polysulfide-perchlorate. Polyvinyl chloride-plasticizer-perchlorate systems were then developed which made use of the plastisol technique. Compression molded propellants of another variety were the next development resulting from the fact that rubber could be mixed with an oxidant and the mass formed under heat and pressure into a strong, well-consolidated grain. These molding techniques, however, limited the size of the charge which could be formed because the total force exerted over the grain surface was limited to the size of the mold and the force capacity of the compression molding apparatus. Large diameter solid grains suitable for first stage ballistic missiles or space boosters could, however, be fabricated with the cast-composite manufacturing methods which called for a liquid fuel to be mixed with a solid oxidizer. When the solids were thoroughly dispersed, the semi-solid, pourable "batter" could then be cast into a rocket motor cavity. By cooling, or by controlled chemical reactions within the fuel the mixture would set up or cure to a solid. The liquid fuel thus became a binder, that is, a component which performed two functions; first, imparted good mechanical properties to the propellant and second, burned as a fuel. In practice, the mechanical properties of a solid propellant improves as the ratio of binder to oxidizer increases. However, in most systems, peak energetics occurs at the 9-11 percent by weight binder level whereas minimum acceptable physical properties are first achieved at the 14 to 16 percent level. The importance of reliable mechanical properties can be illustrated by showing that most operational systems accept the sacrifice in energy and operate at the 14 to 16 percent binder level. The effect of binder level on energetics is shown in Figure 1, a plot of energy (as specific impulse) vs binder level.

A major advance in propellant technology occurred when it was discovered that metallic fuels could be incorporated into the binder-oxidizer mixture to give higher energy as well as higher density propellants without affecting the mechanical properties of the system (i. e. without lowering the allowable binder level). This paradoxical situation can be understood if it is realized that a hydrocarbon-oxidizer system is balanced to give carbon monoxide, carbon dioxide and steam as combustion products. The metallic

additive is oxidized by the steam and therefore does not require additional oxidant. In the case where aluminum is added to a hydrocarbon-ammonium perchlorate system, the combustion proceeds in the following manner:

$$NH_4ClO_4 + (CH_2)_n + 2Al \longrightarrow 1/2\ N_2 + CO + 5/2\ H_2 + Al_2O_3 + HCl$$
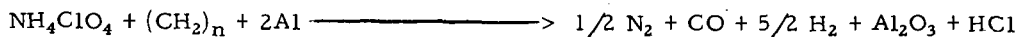
The formation of hydrogen gas as a combustion product is very desirable because performance of a system is proportional to the factor

$$\sqrt{\frac{\Delta H}{\overline{M}}}$$

where ΔH is the heat released in combustion and $\overline{M}$ is the mean molecular weight of the combustion products. Figure 2 illustrates the performance improvement found in these metallized systems and shows, as well, the fact that the binder level for optimum performance stays the same as it would be in a metal-free system. The example shown is for a typical hydrocarbon-aluminum-ammonium perchlorate system.
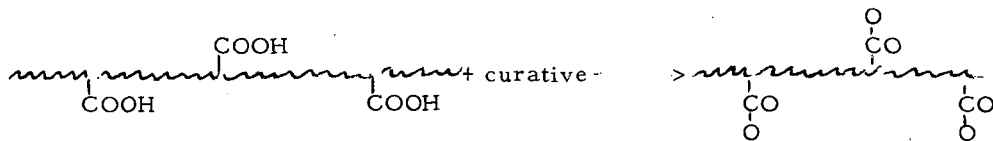
With the foregoing background it is now possible to proceed with a discussion of the directions that research has taken in the development of new and improved binder systems. Two major efforts can be categorized in this review. The first was motivated by attempts to improve the physical properties of propellants while maintaining their energetics. The second effort is a straightforward attempt to increase energetics while maintaining acceptable mechanical properties.

For a treatment of binder developments leading to the improvement of physical properties one must recognize that all hydrocarbon binders are equal in energetics. Nevertheless the binding capability of a hydrocarbon polymer will vary with small changes in its geometrical structure. Although there was enough scientific information available early in the development of solid propellants to aid in the selection of the best polymeric structures, the actual developments followed a typical evolutionary route.
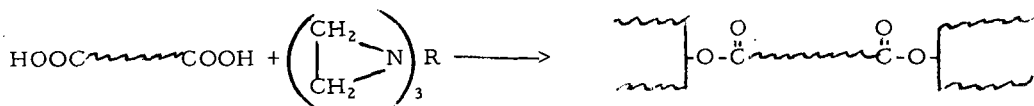
The earliest cast, composite binder to be used was molten asphalt. This material was heated until it formed a fluid melt, was mixed with oxidant and the heated mixture cast into a motor cavity and allowed to cool. This system was a poor one because of the limited temperature range, the low solids content which could be formulated, and the poor mechanical properties of highly loaded asphalt. A chemically cured system was then introduced when acrylate monomers were mixed with oxidizer and curative. The mixture could be cast, heated to cure temperature and the acrylate polymerized to give a well consolidated grain. The basic deficiencies encountered in this type of system were the exotherm, at times uncontrollable, during cure and the shrinkage of the solid due to the fact that the polymer had an appreciably higher density than the monomer. Furthermore, the acrylates used were not particularly rubbery so that their mechanical properties were only suitable for small grains. The addition of a polyfunctional unsaturate, such as divinyl benzene, to the acrylate acted as a cross-linking agent in this system.

The next advance in solid propellant binders came from the use of partially polymerized liquids which retained functionality for subsequent curing. The best example of such a system is the controlled molecular weight polymers obtained from butadiene and acrylic acid. This system is still a liquid of 200 to 300 poise viscosity at 25^0C at 2000 to 3000 molecular weight. It is sufficiently fluid at processing temperatures (50 to 60^0C) to allow formulation with 80 to 85 percent by weight of solids and still give a castable mix. Curatives of the epoxy or imine type are added to the mix and the system is
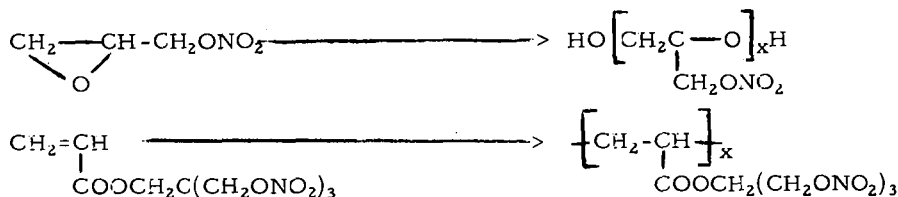
allowed to cure over a period of 3 to 24 hours to a resilient solid. The system can be represented in the following manner:

$$\underset{\underset{\text{COOH}}{|}}{\text{COOH}} \quad \underset{\underset{\text{COOH}}{|}}{\text{COOH}} \quad + \text{ curative } \rightarrow \quad \underset{\underset{O}{\overset{|}{\underset{O}{\text{CO}}}}}{\overset{O}{\overset{||}{\text{CO}}}} \quad \underset{\underset{O}{\overset{|}{\text{CO}}}}{\overset{|}{\text{CO}}}$$
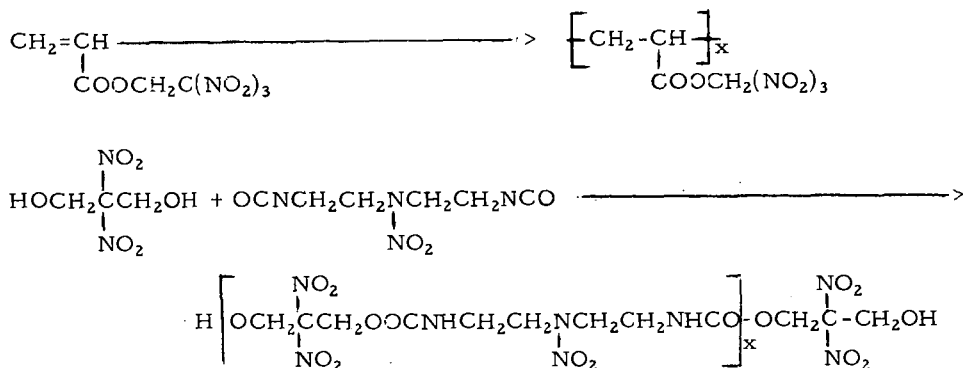
From a theoretical point of view the mechanical properties of a polymeric system can be optimized if the cross-links are introduced in a regular manner and not in a random fashion as shown in the previous equation. It was therefore considered a desirable development when controlled molecular weight systems were made available which had their functional groups only at the ends of chains. These systems were cured with tri and polyfunctional curing agents of the trisimine type. The following equation illustrates the curing reaction of a carboxy terminated hydrocarbon polymer.

$$\text{HOOC}\sim\sim\text{COOH} + \left(\underset{\underset{\text{CH}_2}{|}}{\overset{\text{CH}_2}{|}}\text{N}\right)_3 R \longrightarrow \quad \underset{}{\Big]}\text{O}-\overset{O}{\overset{||}{\text{C}}}\sim\sim\sim\overset{O}{\overset{||}{\text{C}}}-\text{O}\Big[$$
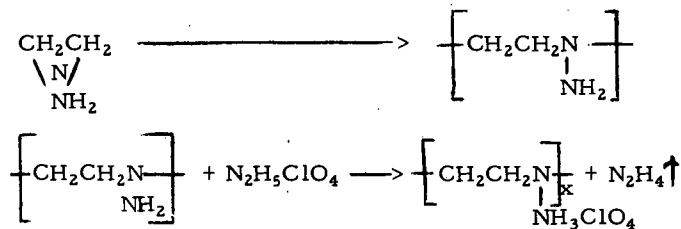
Various attempts have been made to reduce the solids loading of binders by incorporating oxygen into the polymeric structure. In order to maintain the oxidizing potential of the binder oxygen, groups such as the nitrato and nitro were first used. Actually the earliest solid propellant binder was cellulose nitrate plasticized with the nitrate ester nitroglycerin. This system however, was not castable in the conventional sense in that unwarranted extensive development work would be required. Other nitrate ester systems were studied such as that derived from glycidyl nitrate and petrin acrylate.

$$\underset{\underset{O}{\diagdown\diagup}}{\text{CH}_2\text{—CH-CH}_2\text{ONO}_2} \longrightarrow \text{HO}\left[\underset{\underset{\text{CH}_2\text{ONO}_2}{|}}{\text{CH}_2\text{C—O}}\right]_x\text{H}$$

$$\underset{\underset{\text{COOCH}_2\text{C(CH}_2\text{ONO}_2)_3}{|}}{\text{CH}_2=\text{CH}} \longrightarrow \left\{\underset{\underset{\text{COOCH}_2(\text{CH}_2\text{ONO}_2)_3}{|}}{\text{CH}_2\text{-CH}}\right\}_x$$

These nitrate systems were found to suffer from the same thermal instability characteristics encountered in the double base systems so that incorporation of oxygen as the more stable nitro groups appeared attractive. Both addition and condensation nitro polymers were prepared as illustrated in the following equations:
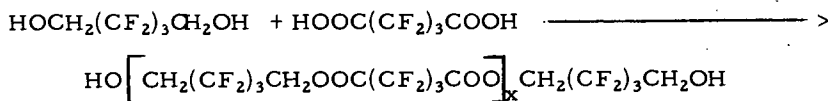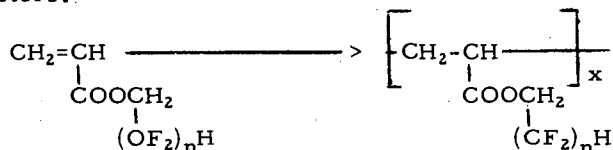
$$\underset{\underset{\text{COOCH}_2\text{C(NO}_2)_3}{|}}{\text{CH}_2=\text{CH}} \longrightarrow \left[\underset{\underset{\text{COOCH}_2(\text{NO}_2)_3}{|}}{\text{CH}_2\text{-CH}}\right]_x$$

$$\underset{\underset{\text{NO}_2}{|}}{\overset{\overset{\text{NO}_2}{|}}{\text{HOCH}_2\text{CCH}_2\text{OH}}} + \text{OCNCH}_2\text{CH}_2\underset{\underset{\text{NO}_2}{|}}{\text{NCH}_2\text{CH}_2\text{NCO}} \longrightarrow$$

$$\text{H}\left[\underset{\underset{\text{NO}_2}{|}}{\overset{\overset{\text{NO}_2}{|}}{\text{OCH}_2\text{CCH}_2\text{OOCNHCH}_2\text{CH}_2}}\underset{\underset{\text{NO}_2}{|}}{\text{NCH}_2\text{CH}_2\text{NHCO}}\right]_x \underset{\underset{\text{NO}_2}{|}}{\overset{\overset{\text{NO}_2}{|}}{\text{OCH}_2\text{C-CH}_2\text{OH}}}$$

Another energetic oxygen rich binder was prepared which incorporates the perchlorate group as an amine salt.

$$CH_2CH_2 \overset{\diagdown N \diagup}{\underset{NH_2}{}} \longrightarrow \left[CH_2CH_2N \underset{NH_2}{} \right]$$

$$\left[CH_2CH_2N \underset{NH_2}{} \right] + N_2H_5ClO_4 \longrightarrow \left[CH_2CH_2N \underset{NH_3ClO_4}{} \right]_x + N_2H_4 \uparrow$$

Recently, the discovery of organic compounds which possess the difluoramino group (RNF_2) has prompted study of polymers which have high concentrations of NF_2.

$$\left[CH_2\underset{F_2N}{CH} - \underset{NF_2}{CH} - CH_2 \right]_x$$
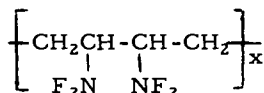
In addition, fluorocarbon polymers, which can be considered as low energy oxidizing binders have been investigated because they are compatible with reactive oxidants and are of high density. Examples of such systems are the fluoroalkyl acrylates and fluoropolyesters.

$$CH_2=\underset{\underset{(OF_2)_nH}{COOCH_2}}{CH} \longrightarrow \left[CH_2-\underset{\underset{(CF_2)_nH}{COOCH_2}}{CH} \right]_x$$

$$HOCH_2(CF_2)_3CH_2OH + HOOC(CF_2)_3COOH \longrightarrow$$

$$HO \left[CH_2(CF_2)_3CH_2OOC(CF_2)_3COO \right]_x CH_2(CF_2)_3CH_2OH$$

Paralleling the oxidizer binder developments has been work on energetic fuel binders. In this way the binder can be looked upon not only for its mechanical properties but also for its truly energetic contributions to the solid propellant. One example of such an approach was work carried out to incorporate the high heat of formation acetylenic group into the polymer structure. A castable system was prepared based upon the readily available acetylenic monomer butynediol and its reaction with formaldehyde.

$$HOCH_2C{\equiv}CCH_2OH + CH_2O \longrightarrow HO \left[CH_2C{\equiv}CCH_2OCH_2O \right]_x$$

Also, polymers were prepared by the oxidative coupling of dipropargyl ether

$$HC{\equiv}CCH_2OCH_2C{\equiv}CH + O_2 \overset{Cu^+}{\longrightarrow} \left[C{\equiv}CCH_2OCH_2C{\equiv}C \right]_x + H_2O$$
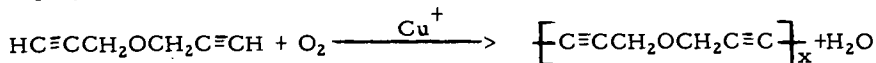
and the vinyl polymerization of isopropenylacetylene.

$$CH_2=\underset{\underset{C{\equiv}CH}{\overset{CH_3}{|}}}{C} \longrightarrow \left[CH_2-\underset{\underset{C{\equiv}CH}{\overset{CH_3}{|}}}{C} \right]_x$$
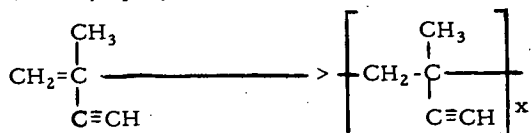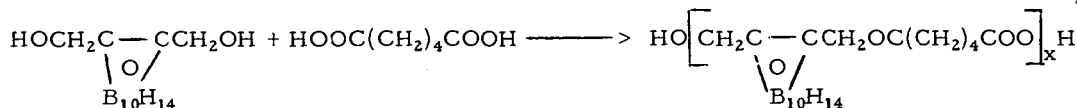
A successful effort was made in incorporating boron hydrides into polymer systems. The early studies made use of decaborane and its simple alkyl derivatives. The difunctionality of decaborane towards Lewis bases allowed the formation of coordination polymers of the following type:

$$NC(CH_2)_4CN + B_{10}H_{14} \longrightarrow H_2 + \left[NC(CH_2)_4CNB_{10}H_{12} \right]_x NC(CH_2)_4CN$$
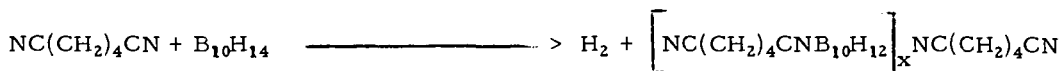
These polymers tended to be resinous and were also still strong reducing agents. Therefore they could not be safely formulated with oxidants. A major development took place when the dicarbaclovododecaborane (carboranes) compounds were discovered because these materials were extremely stable and were organophilic in character. The basic reaction for carborane formation is described in the following equation.

$$B_{10}H_{14} + R_1C\equiv CR_2 \xrightarrow[\text{Base}]{\text{Lewis}} 2H_2 + R_1C \underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{\overline{\qquad}} CR_2$$
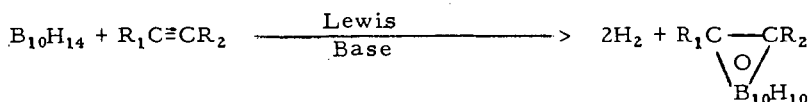
A wide range of monomers and polymers were synthesized; of these the polyester system, shown in the following equations, was most intensively developed.

$$HOCH_2C \underset{\underset{B_{10}H_{14}}{\diagdown O \diagup}}{\overline{\qquad}} CCH_2OH + HOOC(CH_2)_4COOH \longrightarrow HO\left[CH_2C \underset{\underset{B_{10}H_{14}}{\diagdown O \diagup}}{\overline{\qquad}} CCH_2OC(CH_2)_4COO \right]_x H$$

By adjusting the ratios of monomers it was possible to prepare OH, COOH and mixed terminal groups. The polymers were chain extended and cross-linked with isocyanates to give resilient rubbery products.

Other carborane systems which were studied included the copolymer of isopropenyl carborane with butadiene and a carboranyl acrylate, both of which are shown in the following equations.
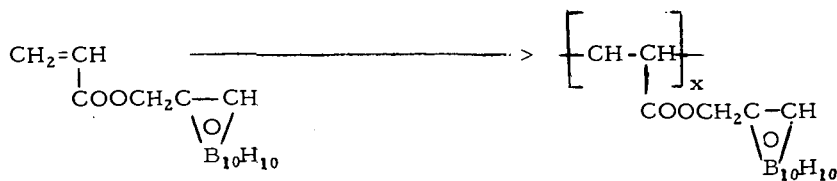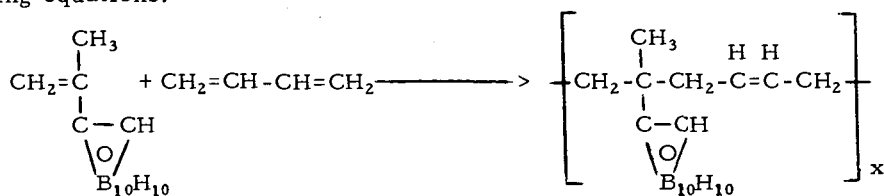
It can be seen from a review of the pertinent synthetic chemistry used for binder research that significant scientific contributions fell out of this work. Most of the advanced systems developed, however, have found very limited application to solid propulsion due to such factors as thermal and shock sensitivity, lower energy than originally calculated, high cost and lack of availability of chemicals, the physical properties of the polymers prepared.

Isp vs. % Binder for a $-(CH_2)_{\overline{x}}$/AP Propellant
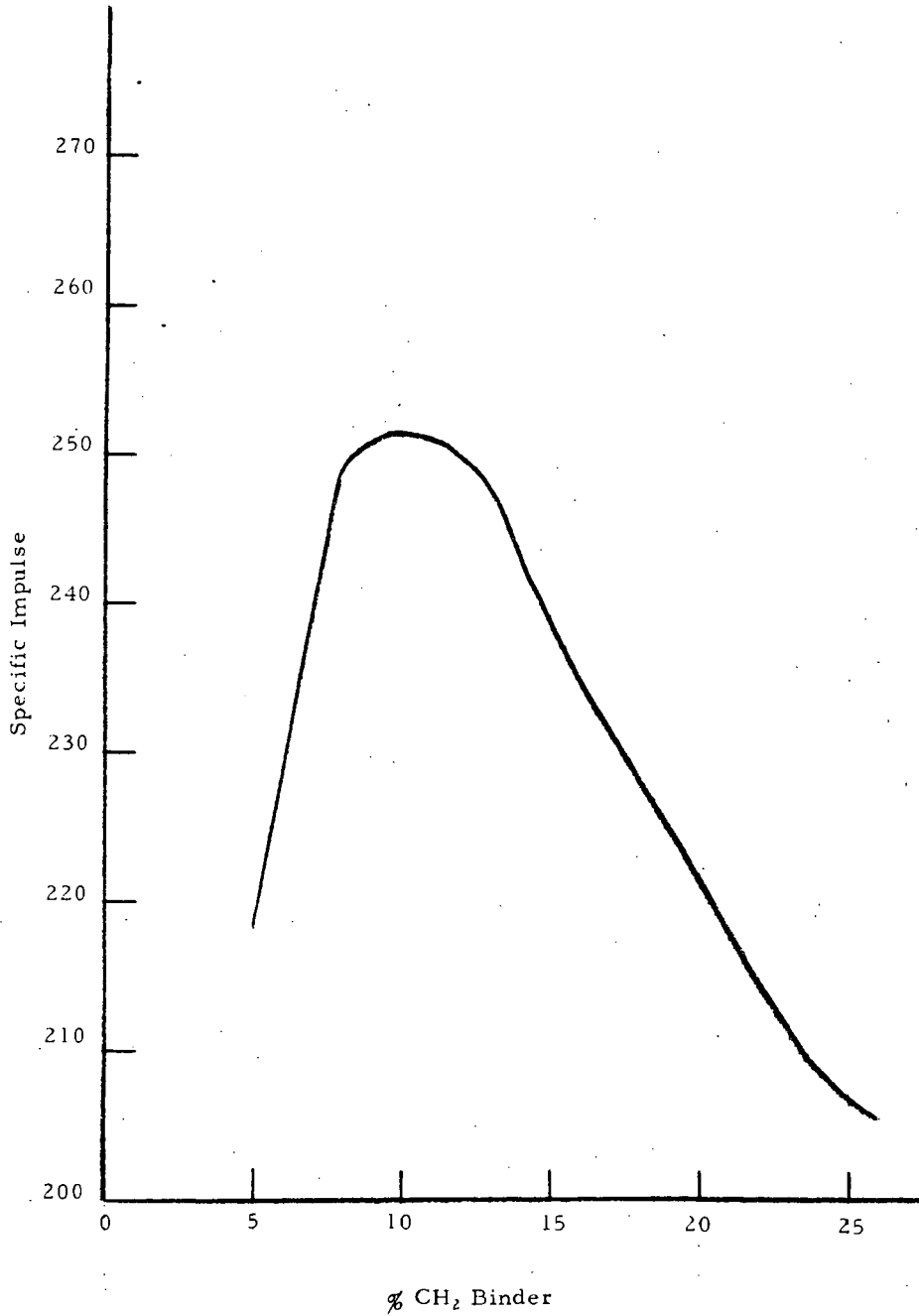

% CH_2 Binder

Figure 1

I_{sp} vs. % Binder at 3 Al Levels for a $-(CH_2)_x$ -Al-AP Propellant

Figure 2